

THE UNIVERSITY OF CHICAGO

## BACKGROUND OF THE INVENTION

This invention relates to a process for producing a coating film which can be used as protective coatings for houstop water-proofing, architectures such as floors and external walls of buildings, building materials, sports facilities such as tennis courts and athletic sports stadiums, as well as structures for display installed outdoors, such as road-signs, automobiles, domestic electric appliances, wood works, plastics moldings and printed matters, and further as surface coating materials for substances unstable to light and has excellent weather resistances required for long-term outdoor use such as gloss retainability, resistance to discoloration and resistance to cracking, and also to a coating material which can give the above-mentioned film.

As to a method for improving the weather resistance of coating materials, there have hitherto been known two-component coating compositions containing a compound having an ultraviolet absorbing ability (hereinafter referred to as ultraviolet absorptive compound) incorporated into the composition. Such coating compositions are excellent in weather resistance and, since they are of two-component system, can form coating film excellent in such physical

properties as adhesiveness and coating film strength;  
so that they have been used as top coat for housetop  
water-proofing and external walls of buildings,  
building materials, sports facilities, and the like.

5           In particular, when an acrylic polyol is used  
as the binder of the coating material and an isocyanate  
prepolymer is used as the curing agent thereof, the  
resulting coating composition can form a coating film  
excellent in weather resistance, gloss, chemical  
10 property and mechanical strength, and has been  
generally used as a coating material for outdoor use.  
However, the above-mentioned coating composition has a  
shortcoming in that when the coating film obtained is  
used for a long period, a bleeding phenomenon, wherein  
15 the ultraviolet absorptive compound bleeds out to the  
surface, occurs and hence the beneficial effect of the  
compound does not last long.

To overcome the above-mentioned shortcoming,  
some attempts have been made to fix the ultraviolet  
20 absorptive compound into the coating composition, and a  
method has been proposed wherein a polymerizable  
ultraviolet absorptive compound is polymerized in an  
acrylic polyol (JP-A-9-3393).

As to the curing agent, further, a coating  
25 composition incorporated with a product obtained by  
bonding an ultraviolet absorptive compound into an  
isocyanate has been disclosed (JP-B-47-29199).

With regard to the ultraviolet absorptive

compound in the coating material, however, attention has been attracted only to the amount of the compound incorporated into the coating material, and much remains unknown with respect to the relation of the

5 ultraviolet absorbing abilities of the ultraviolet absorptive compound as molecular extinction coefficient and absorbing wavelength region with the weather resistance and the relation between the amount of the ultraviolet absorptive compound present in the coating

10 film after coating and the weather resistance. Thus, though it is already known that the use of an expensive ultraviolet absorptive compound is effective, it is still unclear how to make efficient use of such a compound, and no suggestion has yet been made of a

15 design technique which can control the weather resistance as desired.

#### SUMMARY OF THE INVENTION

The object of this invention is to provide a process for producing a coating composition excellent

20 in long-term weather resistances including gloss retainability and resistance to discoloration in long period outdoor use which comprises, in a two-component curable coating material, chemically bonding, an ultraviolet absorptive compound to the binder or the

25 curing agent such that its ultraviolet absorbing ability is not impaired, to make the dry coating film after coating contain a specified amount of the

compound. For this purpose, in this invention, the relation between the amount of an ultraviolet absorptive compound used and the weather resistance is examined, from which a design technique for obtaining  
5 weather resistance which meets the performance requirements of the coating material is obtained, and the above-mentioned process can be provided based on the design technique.

The present inventors have made extensive  
10 study on a process for producing a coating composition which can retain good weather resistance for a long period. As a result, the inventors have found out conditions for minimizing ultraviolet degradation by incorporating into a coating composition a product  
15 obtained by chemically bonding an ultraviolet absorptive compound to a binder or a curing agent so as to make the dry coating film after coating contain a specified amount of the compound, and resultantly succeeded in obtaining a coating film excellent in  
20 weather resistance. This invention has been thus accomplished.

According to this invention, there are provided a process for producing a weather resistant coating film which can keep a gloss retention of 80% or  
25 more for 1000 hours or more in an accelerated weathering test by a carbon sunshine weather-o-meter by preparing a weather resistant coating material comprising a binder and a curing agent as main

constituents and coating an article to be coated with the coating material, followed by drying, which process comprises

chemically bonding an ultraviolet absorptive  
5 compound having the maximum value of light absorption spectrum in a wavelength region shorter than 380 nm and having a molecular extinction coefficient at the absorption maximum wavelength of 5,000 to 50,000 to either or both of the binder and the curing agent  
10 constituting the coating material,

preparing a coating material with the above-mentioned bonding and constitution of the coating material being designed such that when the coating material is coated on an article and dried, the  
15 concentration C (mol/L) of the residual group of the ultraviolet absorptive compound in the dry coating film may satisfy the expression

$$\epsilon dC \geq 129 \cdot \log \tau - 367,$$

wherein  $\epsilon$  is the molecular extinction coefficient of  
20 the residual group of the above-mentioned compound in the dry film, d is the thickness (cm) of the dry film when in use, and  $\tau$  is the time (hr) of exposure in the accelerated weathering test that shows a gloss retention of 80% or more which is determined according  
25 to the requirements of intended uses, and

coating the coating material on the article,

followed by drying, so that the thickness of the dry coated film may become the above-mentioned d, and a coating material which can provide the above-mentioned film.

## 5 BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing the ultraviolet transmittance of each coating film.

Fig. 2 shows the absorption spectrum of a functional group residue having ultraviolet absorbing  
10 ability.

Fig. 3 is a graph showing a relation between the amount of the functional group of an ultraviolet absorptive compound and the absorbance.

Fig. 4 is a graph showing a relation between  
15 absorbance and gloss retention.

Fig. 5 is a graph showing a relation between the amount of a functional group and gloss retention.

Fig. 6 is a graph showing a relation between absorbance and gloss retention.

Fig. 7 is a graph showing a relation between  
20 the amount of the functional group residue having ultraviolet absorbing ability in the coating film and the gloss retention.

Fig. 8 is a graph showing a relation between  
25 absorbance and weather resistance.

Fig. 9 is a graph showing a relation among the concentration and the molecular extinction

coefficient of an ultraviolet absorptive compound residual group in the coating film, the thickness of dry coating film and the exposure time.

#### DETAILED DESCRIPTION OF THE INVENTION

5           This invention is described in detail below.

          In this invention, the ultraviolet absorptive compound having the maximum value of its light absorption spectrum in a wavelength region shorter than 380 nm and having a molecular extinction coefficient at  
10 the absorption maximum wavelength of 5,000 to 50,000 (said compound being hereinafter referred to simply as ultraviolet absorptive compound) is used singly or in a combination of two or more thereof and is bonded into the binder or the curing agent such that the  
15 ultraviolet absorbing ability of the ultraviolet absorptive compound may not be impaired, in other words, the compound may be bonded, through its group or moiety other than that having the ultraviolet absorbing ability, into the binder or the curing agent, and the  
20 group or moiety having the ultraviolet absorbing ability may remain unreacted or unchanged. In this invention, further, the amount of the ultraviolet absorptive compound to be bonded is determined such that when the coating material is coated and dried the  
25 concentration C (mol/L) of the ultraviolet absorptive compound residual group in the dry coating film may satisfy the above-mentioned expression, and the



constitution of the coating material, that is, the  
compounding amounts of the binder and the curing agent  
to which the ultraviolet absorptive compound has been  
bonded, is determined so as to satisfy the above-  
5 mentioned expression.

The ultraviolet absorptive compound used in  
this invention may be, for example, an ultraviolet  
absorptive compound having an active hydrogen and an  
ultraviolet absorptive compound having a polymerizable  
10 vinyl group.

The ultraviolet absorptive compound having an  
active hydrogen may be, for example, benzotriazole type  
compounds having an active hydrogen, such as 2-(2'-  
hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-  
15 5'-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-t-  
butyl-5'-methylphenyl)-5-chlorobenzotriazole and 2-(2'-  
hydroxy-4'-octoxyphenyl)benzotriazole; and benzophenone  
type compounds having an active hydrogen, such as 2-  
hydroxy-4-octoxybenzophenone, 2-hydroxy-4-  
20 ethoxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-  
hydroxy-4-octoxy-2'-chloro-benzophenone and 2-hydroxy-  
4-octoxy-3'-methyl-benzophenone; used each alone or in  
a combination thereof.

The ultraviolet absorptive compound having a  
25 polymerizable vinyl group may be, for example,  
benzotriazole type compounds having a vinyl group, such  
as 2-[2'-hydroxy-5'-(methacryloyloxymethyl)phenyl]-2H-  
benzotriazole, 2-[2'-hydroxy-5'-(methacryloyloxyethyl)-

phenyl]-2H-benzotriazole, 2-[2'-hydroxy-5'-t-butyl-3'-(methacryloyloxyethyl)phenyl]-2H-benzotriazole and 2-[2'-hydroxy-5'-(methacryloyloxyethyl)phenyl]-5-chloro-2H-benzotriazole) and benzophenone type compounds  
5 having a vinyl group, such as 2-hydroxy-4-(3-acryloxy-2-hydroxypropoxy)benzophenone, 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone and 2'-dihydroxy-4-(3-methacryloxy-2-hydroxypropoxy-benzophenone; used each alone or in a combination  
10 thereof.

For chemically bonding the ultraviolet absorptive compound to the binder or the curing agent in the coating material, it is preferable to polymerize an ultraviolet absorptive compound having a  
15 polymerizable vinyl group with another monomer and/or prepolymer each having a polymerizable vinyl group, or to make an ultraviolet absorptive compound having an active hydrogen react on an isocyanate prepolymer and/or isocyanate monomer each having at least two free  
20 isocyanate groups. By chemically bonding the ultraviolet absorptive compound to the binder or the curing agent in the coating material, coating film excellent in weather resistance can be provided. The most preferable method in using a binder or a curing  
25 agent to which an ultraviolet absorptive compound has been bonded is to use an acrylic polyol as the binder and, at the same time, to use a nonyellowing isocyanate as the curing agent.

More specifically, the ultraviolet absorptive compound having a polymerizable vinyl group, which is a constituent of the acrylic polyol (binder) to which the above-mentioned ultraviolet absorptive compound has  
5 been bonded, may be, for example, a benzotriazole type compound having a vinyl group, such as 2-[2'-hydroxy-5'-(methacryloyloxymethyl)phenyl]-2H-benzotriazole, 2-[2'-hydroxy-5'-(methacryloyloxyethyl)phenyl]-2H-benzotriazole, 2-[2'-hydroxy-5'-t-butyl-3'-  
10 (methacryloyloxyethyl)phenyl]-2H-benzotriazole and 2-[2'-hydroxy-5'-(methacryloyloxyethyl)phenyl]-5-chloro-2H-benzotriazole; and a benzophenone type compound having a vinyl group, such as 2-hydroxy-4-(3-acryloxy-2-hydroxypropoxy)benzophenone, 2-hydroxy-4-(3-  
15 methacryloxy-2-hydroxypropoxy)benzophenone and 2'-dihydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone; used each alone or in a combination thereof.

The unsaturated monomer component having a  
20 hydroxyl group which serves as another constituent may be, for example, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and caprolactone-modified hydroxy (meth)acrylate, used each alone or in a combination thereof.

25 Another polymerizable monomer which is another constituent may be, for example, cyclohexyl (meth)acrylate, methylcyclohexyl acrylate, t-butylcyclohexyl (meth)acrylate, methyl (meth)acrylate,

ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl  
(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)-  
acrylate, sec-butyl(meth)acrylate, t-butyl(meth)-  
acrylate, isopentyl(meth)acrylate, neopentyl(meth)-  
5 acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate,  
octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate,  
stearyl(meth)acrylate, benzyl(meth)acrylate,  
dimethylaminomethyl acrylate, diethylaminomethyl  
acrylate, dibutylaminomethyl acrylate,  
10 dihexylaminomethyl acrylate, styrene,  $\alpha$ -methylstyrene,  
vinyltoluene, vinylidene chloride, vinyl acetate,  
acrylic acid, maleic acid, itaconic acid, 2-  
acryloyloxyethylsuccinic acid and 2-acryloyloxyethyl-  
phthalic acid, used each alone or in a combination  
15 thereof.

As other constituents, there may be used, if  
necessary and desired, a light stabilizer, such as 4-  
(meth)acryloyloxy-2,2,6,6-tetramethylpiperidine, 4-  
(meth)acryloylamino-2,2,6,6-tetramethylpiperidine, 4-  
20 (meth)acryloyloxy-1,2,2,6,6-pentamethylpiperidine, and  
4-(meth)acryloylamino-1,2,2,6,6-pentamethylpiperidine,  
each alone or in a combination thereof.

The method of polymerization used in  
copolymerizing the monomer composition comprising the  
25 above-mentioned constituents for preparing the binder  
is not particularly limited, but it is preferably  
solution polymerization.

The solvent used in the copolymerization may

be, for example, aromatic hydrocarbons, such as toluene and xylene; ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters, such as ethyl acetate and butyl acetate; cellosolve acetate and  
5 propylene glycol monomethyl ether acetate; used each alone or in a combination thereof.

A polymerization initiator is used in copolymerizing the monomer composition. Polymerization  
10 initiators generally used are, for example, those of azo type, such as azobisisobutyronitrile, and those of peroxide type, such as benzoyl peroxide; which may be used each alone or in a combination thereof.

The ultraviolet absorptive compound having an active hydrogen which is a constituent of the curing  
15 agent to which the above-mentioned ultraviolet absorptive compound has been bonded may be, for example, a benzotriazole type compound, such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-t-  
20 butyl-5'-methylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole; and a benzophenone type compound, such as 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-ethoxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxy-2'-  
25 chlorobenzophenone and 2-hydroxy-4-octoxy-3'-methylbenzophenone; used each alone or in a combination thereof.

The isocyanate compound used as another

constituent may be, for example, nonyellowing isocyanates, such as hexamethylene diisocyanate, isophorone diisocyanate and cyclohexylmethane diisocyanate; their isocyanurates, biurets and  
5 trimelthylolpropane adducts; and the adducts thereof with compounds having an active hydrogen, such as amines, carboxylic acids, alcohols, and the derivatives thereof. They may be used each alone or in a combination thereof.

10 In reacting the isocyanate compound with the ultraviolet absorptive compound containing an active hydrogen, there may be added to these constituents a compound having an active hydrogen, e.g., amines, carboxylic acids, alcohols, and the derivatives  
15 thereof, each alone or in a combination thereof, whereby the chemical characteristics and the physical characteristics can be controlled as desired.

The solvents which may be used in reacting the ultraviolet absorptive compound with the isocyanate  
20 are, for example, aromatic ones, such as toluene and xylene, ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone, esters, such as ethyl acetate, butyl acetate and isobutyl acetate, cellosolve acetate and propylene glycol monomethyl ether acetate;  
25 these may be used either singly or in a combination thereof. The use of solvents containing an active hydrogen, e.g., alcohols, should be avoided because such solvents react with isocyanates.

Urethane reaction catalysts may also be used to promote reaction. Such catalysts include, for example, organometallic catalysts, such as dibutyltin diacetate and dibutyltin dilaurate, and amine type catalysts, such as 1,4-diazabicyclo-(2,2,2)octane, triethylamine, N,N,N',N'-tetramethylethylenediamine, triethylenediamine and dimethylaminoethanol. They may be used each alone or in a combination thereof.

Further, according to necessity, any desired isocyanate prepolymer may be mixed, examples of which include isocyanate monomers, such as hexamethylene diisocyanate and isophorone diisocyanate, isocyanurates, biurets, and adducts with a compound having an active hydrogen, such as amines, carboxylic acids, alcohols and the derivatives thereof; they may be used each alone or in a combination thereof.

The method of reaction is not particularly limited, and the reaction may be conducted according to conventional techniques. However, attention should be paid to conduct the reaction preferably by a method which avoids the presence of water. For example, the use of a urethane-grade solvent or the use of a desiccant is advisable. The desiccant which may be used is, for example, tosyl isocyanate, molecular sieve, etc. For obtaining a coating material particularly excellent in weather resistance and physical property in this invention, it is preferable to use isocyanurates or biurets of hexamethylene

diisocyanate. In reacting the ultraviolet absorber with an isocyanate compound, it is preferable to design the reaction such that, on an average, two or more isocyanate groups per molecule remain in the isocyanate composition. When the number of the group is less than two on an average, in the succeeding reaction with the curing agent component the crosslinking tends to be insufficient, leading to unsatisfactory physical properties of the resulting coating material.

The coating material according to this invention may contain, according to necessity, a promoter for reaction with isocyanates, organic solvent, additive, inorganic pigment, organic pigment and body pigment. The reaction promoter may be, for example, organometallic catalysts, such as butyltin diacetate and dibutyltin dilaurate, and amine type catalysts, such as 1,4-diazabicyclo(2,2,2)octane, triethylamine, N,N,N',N'-tetramethylethylenediamine, triethylene-diamine and dimethylaminoethanol, used each alone or in a combination thereof.

The organic solvent may be, for example, aromatic solvents, such as toluene and xylene; ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters, such as ethyl acetate and butyl acetate; cellosolve acetate and propylene glycol monomethyl ether acetate, used each alone or in a combination thereof.

The additive may be various conventional



additives for coating materials, for example, antifoaming agents, dispersants, leveling agents, adhesion improving agent, plasticizers, stabilizers and sedimentation preventing agents, used each alone or in  
5 a combination thereof. The inorganic pigment may be, for example, titanium oxide, zinc white, lead yellow, red oxide, yellow iron oxide, iron black and carbon black. The organic pigment may be, for example, azo type compounds and phthalocyanine type compounds. The  
10 body pigment may be, for example, calcium carbonate, silicon oxide, clay, organic bentonite and silica rock powder. These pigments may be used each alone or in a combination thereof.

In this invention, to attain a sufficient  
15 weather resistance of the coating material, the amount of the functional group of the ultraviolet absorptive compound to be used is determined according to the exposure time that shows a gloss retention of 80% or more which is required by the intended coating film  
20 thickness and intended use of the coating such that when the coating material is coated and dried the concentration C (mol/L) of the residual group of the compound in the dry film may satisfy the empirical expression

25 
$$\epsilon dC \geq 129 \cdot \log \tau - 367$$

wherein  $\epsilon$  is the molecular extinction coefficient of

the said compound residual group in the dry coating film,  $d$  is the thickness (cm) of the dry film when in use and  $\tau$  is the exposure time (hr) in an accelerated weathering test that shows a gloss retention of 80% or more which is required according to the intended use, whereby the object can be achieved.

The article which may be coated by the above-mentioned coating composition is not particularly limited. Articles to be coated include, for example, plastics, such as urethane, FRP (fiber reinforced plastics), polypropylene, polycarbonate and acrylic resins, wood, metal, glass and ceramics. Further, the coating composition may be used for surface protection of such chemical substances as pigments having insufficient weather resistance, protection of printed ink surfaces and surface coating of paper. By applying the coating composition of this invention to the surface of these coated articles, the long-term weather resistance of the coated articles can be recurred.

Thus, the coating composition of this invention can be widely used as a coating material for plastics moldings, domestic electric appliances, metal goods, automobiles, acroplanes, buildings, building materials, sports facilities and wood works.

This invention is described in detail below with reference to Examples and other examples.

Referential Example 1 (Method of preparation of ultraviolet absorber-containing binder (acrylic polyol))

In a flask fitted with a stirrer, dropping  
5 funnel, cooling tube and thermometer were placed 10  
parts by weight of butyl acetate and 10 parts by weight  
of xylene, then brought up to 120° C in nitrogen  
atmosphere, and a polymerizable monomer mixture placed  
in the dropping funnel in the following composition was  
10 added by drops thereto at a constant rate in 2 hours:

	cyclohexyl methacrylate	25 parts by weight
	methyl methacrylate	6 parts by weight
	butyl acrylate	10 parts by weight
	2-hydroxyethyl methacrylate	7 parts by weight
15	acrylic acid	0.3 part by weight
	2-[2'-hydroxy-5'- (methacryloyl)phenyl]- benzotriazole	8 parts by weight
	methacryloylamino-2,2,6,6- tetramethylpiperidine	0.5 part by weight
20	azobisisobutyronitrile	1 part by weight

One hour after completion of the dropwise  
addition, a mixed solution of 0.2 part by weight of  
azobisisobutyronitrile and 10 parts by weight of xylene  
25 was added by drops at a constant rate over 2 hours and,  
after completion of the dropwise addition, the  
resulting mixture was kept at 120° C for 1 hour. After

00864278-052501

cooling, the reaction mixture was diluted with 17.5 parts by weight of xylene to obtain an acrylic polyol (binder) having a viscosity of 30,000 mPa·s, nonvolatile matter content of 56.3% and weight average molecular weight of 31,000.

#### Referential Example 2

The same procedures as in Referential Example 1 were followed to conduct polymerization according to the following composition of polymerizable monomers.

10	cyclohexyl methacrylate	25 parts by weight
	methyl methacrylate	6 parts by weight
	butyl acrylate	10 parts by weight
	2-hydroxyethyl methacrylate	7 parts by weight
	acrylic acid	0.3 part by weight
15	2-[2'-hydroxy-5'-(methacryloyl)-phenyl]benzotriazole	5 parts by weight
	methacryloylamino-2,2,6,6-tetra-	
	methyloperidine	0.5 part by weight
	azobisisobutyronitrile	1.2 part by weight
20	xylene	37.5 parts by weight
	butyl acetate	10 parts by weight

The acrylic polyol (binder) thus obtained had a viscosity of 13,100 mPa·s, nonvolatile matter content of 53.3% and weight average molecular weight of 32,000.

Control Examples 1 and 2

Acrylic polyols (binders) were obtained according to the compositions shown in Table 1 by following the same procedures as in Referential Example 1.

Table 1 Composition and property of acrylic resin

Control Example		1	2
composition	Cyclohexyl methacrylate	25	25
	Methyl methacrylate	6	6
	Butyl acrylate	10	10
	2-Hydroxyethyl methacrylate	7	7
	Acrylic acid	0.3	0.3
	2-[2'-Hydroxy-5'-(methacryloyl)-phenyl]benzotriazole		0.5
	Azobisisobutyronitrile	1.2	1.2
	Xylene	35.5	35.5
	Butyl acetate	10	10
property	Viscosity (mPa·s)	2200	2350
	Nonvolatile matter content (%)	49	50
	Molecular weight (weight average)	30000	31000

The acrylic polyol (binder) obtained in the Referential Example 1 and the acrylic polyol (binder) obtained in Control Example 1 were each formed into a coating film having a thickness of 100  $\mu\text{m}$  after drying, which was then determined for its ultraviolet transmittance with an ultraviolet spectrophotometer. The results of the determination are shown in Fig. 1. Fig. 1 shows the ultraviolet transmittance of each coating film.

Further, the respective absorption spectra of

the binder obtained in Referential Example 1 and the ultraviolet absorptive compound alone before bonding are shown in Fig. 2 each as a relation between the molecular extinction coefficient and the wavelength.

5           The determination was made as follows. For the binder, it was diluted with a spectrally unrelated resin (acrylic polyol described in Referential Example 1) to give a concentration of functional group residue, after bonding, in the coating film of 0.106 m mol/L and  
10 the absorbance was measured at a film thickness of 100  $\mu\text{m}$  to obtain the molecular extinction coefficient. For the ultraviolet absorptive compound before bonding, determination was made by a solution method using a 1 cm cell at a concentration of 0.0619 m mol/L to obtain  
15 the molecular extinction coefficient in the same manner as above.

          The binders obtained in Referential Examples 1 and 2 and the binders obtained in Control Examples 1 and 2 were each formed into a coating film having a  
20 thickness of 100  $\mu\text{m}$  after drying, and the absorbances of the coating films were determined to examine the relation of the amount of the functional group of the ultraviolet absorptive compound per 1  $\text{cm}^2$  with the absorbance. When absorbance is designated A and  
25 transmittance is designated T, absorbance and transmittance are related by  $A = -\log T$ . For absorbances of Referential Examples 1 and 2, determination was made with samples obtained by

diluting the binders prepared in Referential Examples 1 and 2 with a binder having no ultraviolet absorbing ability to 20-fold dilution in terms of solid content, and the absorbances were obtained from the results of determination by calculation. The results thus obtained are shown in Table 2 and Fig. 3. Table 2 shows the relation of the amount of the functional group of the ultraviolet absorptive compound with the absorbance. Fig. 3 shows the relation of the amount of the functional group of the ultraviolet absorptive compound with the absorbance.

Table 2 Relation of amount of functional group of ultraviolet absorptive compound with absorbance

Specimen	Referen- tial Example 1	Referen- tial Example 2	Control Example 1	Control Example 2
Amount of functional group of ultraviolet absorptive compound (mol/L)	0.44	0.29	0	0.032
Absorbance	77	51	0	5.5

Referential Example 3 (Method of preparation of ultraviolet absorber-containing curing agent (isocyanate prepolymer))

In a flask fitted with a stirrer, cooling

09064273.05501  
T0550" B4249360

tube and thermometer were placed 24 parts by weight of butyl acetate, 12 parts by weight of hexamethylene diisocyanurate, 2 parts by weight of 2(2'-hydroxy-5'-methylphenyl)benzotriazole and 0.01 part by weight of dibutyltin dilaurate, then brought up to 70° C in nitrogen atmosphere and allowed to react for 3 hours. After the reaction mixture had been cooled to room temperature, 38 parts by weight of an isocyanate prepolymer (Acrit 8XA-012, a trade name, mfd. by TAISEI CHEMICAL INDUSTRIES, LTD.; nonvolatile matter content: 50%, isocyanate content: 3.1%) was added thereto to obtain an isocyanate prepolymer (curing agent) having a nonvolatile matter content of 43%, viscosity of 20 mPa·s and isocyanate group content of 4.3%.

15 Control Example 3

In a flask fitted with a stirrer, cooling tube and thermometer were stirred 24 parts by weight of butyl acetate and 12 parts by weight of hexamethylene diisocyanurate in nitrogen atmosphere at room temperature for 10 minutes, and 38 parts of an isocyanate prepolymer (Acrit 8XA-012) was added thereto to obtain a composition. Thus, an isocyanate prepolymer with a nonvolatile matter content of 42%, viscosity of 18 mPa·s and isocyanate group content of 5.1% was obtained.



#### Referential Example 4

Pigment dispersion was conducted by using a sand mill and by using the binder resins (acrylic polyols) obtained in Referential Examples 1 and 2 according to the following compositions, to obtain white coating materials.

##### Mill base

	titanium oxide	20 parts by weight
	binder resin	10 parts by weight
10	xylene	5 parts by weight
<hr/>		
	total	35 parts by weight

##### Let down

	mill base	35 parts by weight
	binder resin	50 parts by weight
15	xylene	15 parts by weight
<hr/>		
	total	100 parts by weight

#### Control Example 4

In the same manner as in Referential Example 4 except for using the resins prepared in Control Examples 1 and 2, white coating materials were obtained.

Examples 1 and 2, Comparative Examples 1 and 2

The white coating material of Referential

Example 4 and the isocyanate prepolymer prepared in Referential Example 3, and the white coating material of Control Example 4 and the isocyanate prepolymers prepared in Control Example 3 were respectively

5 compounded so as to give a ratio, NCO group/OH group, of 1/1. The resulting coating materials were each coated on an aluminum plate and dried to give a coating film having a thickness of 150  $\mu\text{m}$  after drying, and subjected to an accelerated weathering test for 2500

10 hours in a carbon sunshine weather-o-meter to determine gloss retention and to examine, from the gloss retention of the respective coating material determined, the relation of absorbance with gloss retention and the relation of the amount of the

15 functional group of the ultraviolet absorptive compound with gloss retention. The results thus obtained are shown in Table 3 and Figs. 4 and 5. Fig. 4 shows the relation of absorbance with gloss retention (1), and Fig. 5 shows the relation of the amount of functional

20 group with gloss retention (1).

Table 3 Composition of coating material and  
result of test

Specimen	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Coating material obtained in Referential Example 4 (part by weight) (Resin is that of Referential Example 1)	100			
Coating material obtained in Referential Example 4 (part by weight) (Resin is that of Referential Example 2)		100		
Coating material obtained in Control Example 4 (part by weight) (Resin is that of Control Example 1)			100	
Coating material obtained in Comparative Example 4 (parts by weight) (Resin is that of Control Example 2)				100
Isocyanate prepolymer obtained in Referential Example 3 (part by weight)	31.4	31.4		
Isocyanate prepolymer obtained in Control Example 3 (part by weight)			26.7	26.7
Amount of functional group of ultraviolet absorptive compound (mol/L)	0.56	0.38	0	0.032
Absorbance (Value determined from Fig. 2)	100.8	68.4	0	5.8
Gloss retention after 2500 hrs of acceleration test in weather-ometer (%)	86	83	21	33

T05250" 84249860

Next, based on the changes of gloss retention of respective coating materials, the points at which gloss retention reached 80% at respective absorbances and at respective amounts of the functional group of the ultraviolet absorptive compound were determined, from which the acceleration time at which gloss retention reaches 80% at any desired absorbance and at any desired amount of the functional group of the ultraviolet absorptive compound was determined. The results thus obtained are shown in Table 4 and Figs. 6-9. Fig. 6 is a graph showing the relation of absorbance with gloss retention (2), Fig. 7 is a graph showing the relation of the amount of functional group with gloss retention (2) and Fig. 8 is a graph showing the relation of absorbance with weather resistance.

Table 4 Change of gloss retention of each coating material

Specimen	Absorbance	Amount of functional group of ultraviolet absorptive compound (mol/L)	Gloss retention (%)				
			500 hrs	1000 hrs	1500 hrs	2000 hrs	2500 hrs
Example 1	100.8	0.56	97	93	91	88	86
Example 2	68.4	0.38	97	92	88	85	83
Comparative Example 1	0	0	79	59	44	31	21
Comparative Example 2	5.8	0.032	85	63	50	41	33

It can be seen that in the group wherein the coating composition obtained by the method of Example 1 is used the weather resistance is improved when the amount of the functional group of the ultraviolet absorptive compound is increased. It can be seen further that when the amount of functional group is 0.38 mol/L, a gloss retention of 80% can be maintained at an acceleration time of 2500 hours, and thus an excellent weather resistance is attained.

To obtain, from the relation shown in Fig. 8, an empirical rule for estimating the value of absorbance at which 80% gloss retention can be attained at an exposure time  $\tau$  determined for intended purposes, the relation of  $\epsilon dC$ , namely absorbance, with  $\log \tau$  was plotted as a graph.

As a result, it has been revealed that the relation shows a good linearity and can be used as an empirical formula for determining C. Thus, the concentration C (mol/L) of the residual group of the ultraviolet absorptive compound to be present in the dry film when the coating material is coated and dried can be determined by the expression.

$$\epsilon dC \geq 129 \cdot \log \tau - 367$$

wherein  $\epsilon$  is the molecular extinction coefficient of the said compound residual group in the dry film, d is the thickness (cm) of the dry coating film when in use

and  $\tau$  is the exposure time (hr) in the accelerated weathering test that shows a gloss retention of 80% or more which is determined according to the requirements of intended uses. This expression is shown by Fig. 9.

5           According to this invention, coating film improved in long-term weather resistance can be obtained without causing deterioration of physical and chemical properties of the film by bonding an ultraviolet absorptive compound to the binder or the  
10   curing agent of the coating material skillfully so that the ultraviolet absorbing ability may not be impaired, thereby to make the dry coating film after drying contain a specific amount of a functional group having ultraviolet absorbing ability. This invention can be  
15   applied to such uses as coating materials and inks wherein great importance is attached to weather resistance.

          According to this invention, the time during which a coating film maintain a gloss retention of 80%  
20   or more in an accelerated test by a carbon sunshine weather-o-meter can be easily lengthened according to the intended use; thus, for example, a long-term weather resistance of 2500 hours or more can be attained.